ACCELERATED AGING OF TIRES, PART II

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ABSTRACT

The purpose of this research is to determine the conditions whereby a new tire can be artificially aged in an accelerated manner, in order to duplicate the actual mechanism of chemical aging observed in field-aged tires. The ultimate goal of the study is to age tires to a desired level, say equivalent to 4 years old, and then test the tires in various durability, high speed and performance tests. The first step was to determine the aging characteristics of field-aged tires, which has been the subject of another paper.[1] For this work, tires were statically aged in ovens. Tires were mounted, inflated, then oven aged continuously at temperatures ranging from 40 °C to 100 °C for various periods of times (from 2 weeks to 12 weeks). Both air and a 50/50 blend of N_2/O_2 were used as the inflation media. The tires were then dissected and analyzed for tensile and elongation properties of the rubber at the end of the steel belts.

The results show that as the temperature was increased from 40 °C to 70 °C, the property degradation of the steel belt rubber accelerated. Shift factors were determined based on time-temperature superposition and the results analyzed by using the Arrhenius methodology. The oven results were similar to the field data, meaning the chemical aging mechanism was the same for both. As the oven temperature increased above 70 °C, degradation reactions began to dominate and the apparent aging mechanism changed.

INTRODUCTION

This paper reports the effects of static oven aging on tire rubber properties. The research is part of a larger effort to develop accelerated aging tests for new tires. The ideal test protocol would achieve two goals: First, after accelerated aging, tires would have chemical/physical properties identical to those found in actual field tires. Second, the amount of test time could be varied (without changing other test parameters) to yield tires of any equivalent age desired. For example, 3 weeks at condition X yields a tire of equivalent field age Y, 5 weeks at condition X yields a tire of equivalent field age Z, *etc*. After aging, tires could then be evaluated in any number of dynamic tests for changes in performance that may have occurred. In this static oven aging study, tires were mounted on rims and inflated to the maximum sidewall pressure listed, then placed in an oven. Two filling gases, air and a 50/50 blend of N_2/O_2, were used. Temperatures ranged from 40 °C to 100 °C at durations from 2 to 12 weeks.

The results from studies conducted on passenger car and light truck tires retrieved from customers in Detroit, MI, USA, show that the steel belt rubber ages oxidatively in the field.[1] Those results are consistent with other findings.[2,3] It is important, then, that any high temperature accelerated aging study also oxidize the subject tires. It is also understood that there are two components of tire aging: 1) chemical aging and 2) mechanical aging. Any tires artificially aged will need to be dynamically tested for structural stability once the static procedure is developed. This sequential approach to tire aging is modeled after the duty cycle of a full-sized spare tire. A typical spare tire statically ages for years under pressure before use. Previous work suggests that this same approach may work for non-spare road tires.[2] For example, evaluations of road tires after 22,000 to 96,000 km of mileage accumulation showed good correlation of wedge rubber tensile properties when compared to tensile properties of identically formulated slab rubber aged in an oven at temperatures from 70 °C-90 °C. Other work shows that only a slight difference in steel belt rubber crosslink density exists between oven aged tires and tires dynamically aged on a 1.7 m road-wheel, but that large differences are observed in the oxidation rate of oven aging inflated vs. uninflated tires.[4]

Tensile and elongation properties were obtained from samples of the wedge rubber located

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between the steel belts in the shoulder (Figure 1). The wedge rubber in a steel belted radial tire is added to help prevent belt edge separations from occurring. It is for this reason that the wedge rubber is one of the most important tire components; the wedge rubber helps determine the durability of a tire. As a tire goes through repeated stress cycling during its lifetime, the strains are the greatest at the belt edge. When the wedge rubber aerobically ages, the material begins to stress harden. This stress hardening lowers the elongation at break and may lower its resistance to crack growth during the stress cycles. This is important because tread and belt delaminations start with cracks growing from the wedge inward between the steel belts. Two different approaches were used in analyzing the tensile data. One approach was based on the work of Ahagon and coworkers, which correlates the strain ratio at break with the modulus at 100% strain.[2,5-6] This approach is particularly useful in distinguishing between different aging mechanisms. The second approach uses the shift factor method developed by Gillen, *et al*. to analyze the kinetics of changes in elongation at break measurements.[7,8,9] It has long been known that elongation at break of rubber is an appropriate measurement when researching the effects of rubber aging.[10] The method will be used to determine if the aging of the wedge rubber is diffusion limited and whether the results obey the Arrhenius equation. The Arrhenius plots will be constructed using the shift factors empirically determined from the plots of normalized strain ratio at break ($\lambda_b = \lambda_{b(t)} / \lambda_{b(0)}$) vs. time.

EXPERIMENTAL

MATERIALS

One tire type was used in the study, a Goodyear Wrangler AP® LT245/75R16 (DOT Code: MD11APWV4102 for Phase 1 and MD11APWV4003 for Phase 2). Tires were mounted and inflated to the maximum pressure listed on the sidewall prior to oven aging: 450 kPa (65 psi). In the case of tires inflated with the 50/50 blend of N_2/O_2, the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 44% O_2. Two separate experiments were conducted. In Phase 1, tires were aged in air circulating ovens for 2, 4, 6, and 8 weeks at 70 °C, 80 °C, 90 °C, and 100 °C. In Phase 2, tires were aged in the same ovens for 3, 6, 9, and 12 weeks at 40 °C, 50 °C, 60 °C, and 70 °C. New tires were analyzed unaged and used as the baseline condition. The ovens were calibrated per ASTM E 145 with an A2LA approved, modified, method for temperature uniformity, consistency, air flow exchanges, and airflow velocity.

PHYSICAL PROPERTIES

Tensile Strength and Elongation. — Samples of the belt wedge rubber (Figure 1), located between belts 1 and 2, were removed from both shoulders of unaged and aged tires and buffed to a uniform thickness of 0.5 to 1.0 mm. Care was taken so that no significant heat was introduced to the samples by the buffing. Specimens were die-cut using an ASTM D 638 Type V dumbbell die and tested per ASTM D 412. Results obtained included stresses at 25%, 50%, 100% strain, and each 100% strain thereafter, ultimate elongation and tensile strength. Samples were tested at 50.8 cm per minute (20 inches/minute).
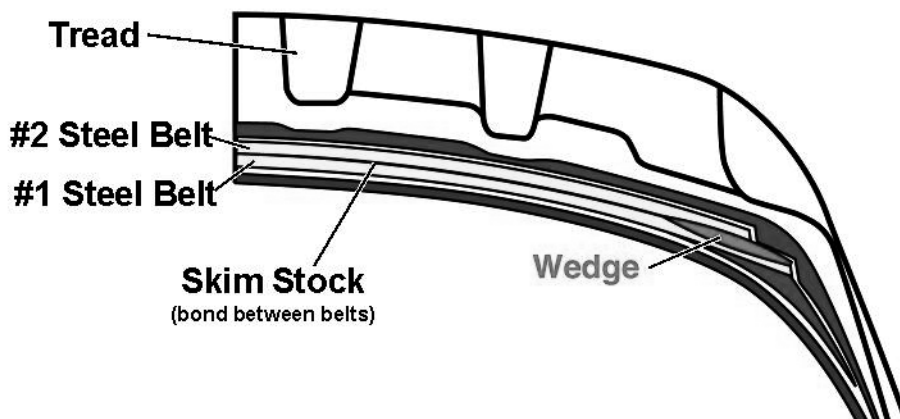
Anatomy of a Typical Radial Tire

FIG. 1. – Tire nomenclature used in this paper.

Reconstruction of Wedge Rubber Chemical Formulation. — An attempt was made to reconstruct the formulation of the wedge rubber. As the reader is undoubtedly aware, chemical reconstruction of a thermoset rubber is difficult and the precise formulation is known only to the compounder. Nevertheless, it is important to understand, at least generally, the chemical make-up of the compound one is studying. Table 1 contains the reconstructed formula. It is also important to realize that the formula represents the rubber as tested, not necessarily as formulated.

TABLE I
CHEMICAL RECONSTRUCTION OF THE WEDGE RUBBER COMPOUND FOUND IN THE TIRES USED IN THIS STUDY

Ingredient	PHR	Extractables	Ash	Volume
Polyisoprene	100	1.0		107.5
Carbon black (N326)	61			33.9
Zinc oxide	6.7		6.7	1.2
Calcium carbonate	1.0	1.0		0.4
Dioctyl adipate	1.0	1.0		1.0
Hydrocarbon oil	5.4	5.4		5.5
Cobalt napthenate	0.5	0.1	0.1	0.5
Wax	1.0	1.0		1.0
Stearic acid	1.0	1.0		1.2
Santoflex 6PPD	2.0	2.0		1.7
Misc. extractables[a]	1.0	1.0		1.1
Santocure NS	1.5	0.3		1.0
Sulfur	2.3			1.2
Total	184.4	12.8	7.8	157.2

Calculated ash content (by wt.)   4.2%
Calculated extractables (by wt.)   6.9%
Calculated carbon black (by wt.) 33.1%
Calculated density (mg/ml)   1.173
[a] Formulation may contain processing aids, waxes, *etc*.

RESULTS AND DISCUSSION

The chemical aging of natural rubber (NR) is generally divided into two types: aerobic and anaerobic. Aerobic aging can be further separated into two mechanisms. Both aerobic kinetic schemes involve the initial step of oxygen cleaving the unsaturated polymer main chain. Depending on the temperature and oxygen concentration, the newly formed main chain radical can either propagate through other double bonds, providing crosslinking, thus increasing the modulus and lowering the strain at break value, or not propagate and rearrange into stable products which lowers both the modulus and the strain-at-break value. It has been shown that the propensity for chain scission to dominate over crosslinking increases as the temperature and/or the oxygen concentration increases.[11,12] Typically, the predominance of anaerobic aging is associated with relatively high temperatures, *e.g.* above 90 °C to 100 °C and is characterized by the breaking and rearranging of the sulfur crosslinks. The physical characteristics of anaerobically aged rubber are lower modulus with retention or even an increase in the strain at break value. The reason for either the aerobic or anaerobic mechanism to dominate in any particular article is design and application dependent. Since oxygen must diffuse through the rubber, a thicker article will exhibit less aerobic aging toward its middle, farther away from the oxygen source. The reason the middle of a thicker rubber article is less affected by oxidation is because oxygen reacts with the rubber along the way, thus starving the interior of oxygen. Even relatively thin samples will show a gradient of oxidation from surface to middle if the temperature is sufficiently high. This mechanism is referred to as Diffusion Limited Oxidation (DLO) and becomes significant when the rate of oxygen consumption in the rubber is greater than the rate which oxygen can be resupplied through diffusion.[13] In developing accelerated aging tests for NR articles, therefore, it is crucial to understand the actual aging mechanism of articles used in the field under normal operating conditions. If that mechanism is aerobic aging of the NR, then care must be taken that the mechanism is duplicated in the laboratory.

In the case of tires, results from studies conducted on samples retrieved from customers in Detroit, MI, USA, show that the steel belt rubber ages oxidatively in the field.[1] This analysis of the wedge rubber properties with respect to aging was initially based on the work of Ahagon, *et.al.*[2,5,6] Tensile and elongation properties were obtained from samples of the wedge rubber located between the steel belts in the shoulder (Figure 1). The aerobic aging of rubber, characterized by a straight line plot of the log of the strain ratio at break vs. the log of the modulus at 100% strain, having a slope of -0.75, should be designated as Type I aging. High temperature aerobic (defined as Type III aging) or possibly anaerobic aging (defined as Type II aging) of the rubber results in data deviating from the straight line. It is important to realize that the slope of –0.75 is an empirically derived number and more than likely dependent on the aging characteristics of the individual compound being studied. Careful reading of the referenced studies does not yield a 'first principles' reason for the slope to be any particular value. Figure 2 is a representation of how data for the various aging types would look in graphic form. Aerobically aging NR typically hardens, leading to lower elongation at break, yielding a prediction of a negative slope for the given data treatment.
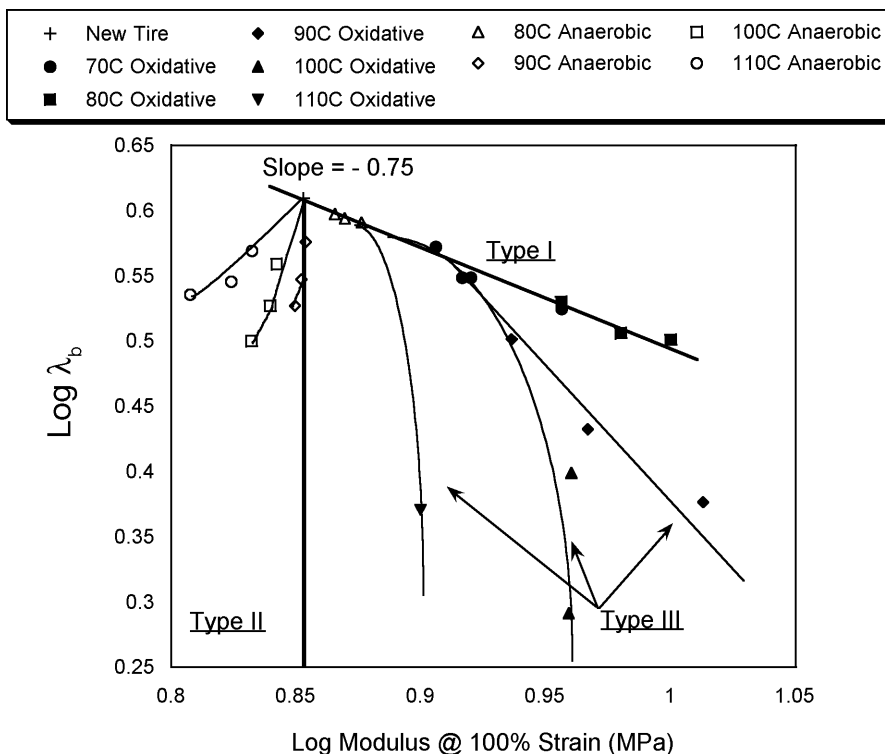
Fig. 2. – Data analysis ('Ahagon Plot') used to understand aging mechanism of wedge rubber.
The plot is of the log of the strain ratio at break vs. the log of the modulus at 100% strain.

The wedge region is usually in the thickest part of the tire. For that reason, it is especially important to carefully follow the mechanism of aging in any development of an accelerated aging test. A balance between temperature and oxygen concentration must be maintained or else Type II and Type III aging can occur. Investigation into accelerated aging was done by using mounted, inflated tires statically aged in ovens at various times and temperatures. The reason behind mounting the tires was twofold: i) to more closely duplicate the actual condition of a tire in the field; and, ii) because it has been reported that the inflating air permeates the halobutyl innerliner and is the source of oxygen for the belt package region of the tire.[14] Oven aging was chosen because it is well known that increased temperatures accelerate oxidative aging of NR. Two filling gases, air and a 50/50 blend of N_2/O_2, were used. In the case of tires inflated with the 50/50 blend of N_2/O_2, the atmospheric air present was not purged; the blend was added on top of it yielding a tire cavity concentration of approximately 44% O_2.

Preliminary results for the Phase 1 study were presented earlier and part of those findings are included for completeness.[15] Data was taken at 70 °C for both groups to allow comparison. It is well known that tires are made in batches and that slight differences can exist between the batches. Even though the tires are the same brand, size and chemical make-up (as shown in the Experimental section), slight differences in properties can be observed due to variations in the manufacturing process. The two phases of the current study have tires representing two different weeks of manufacture, according to the date code contained in the DOT markings on the tire. Each phase consists of tires from one week of manufacture.

Figure 3 is an 'Ahagon' plot for tires aged at 70 °C and inflated with air. Figure 4 is the same plot for tires inflated with 50/50 N_2/O_2. The results of the plots are the same for both inflation media. The tires studied in Phase 2 are offset from the data for Phase 1 and have a slightly lower

slope (approximately –0.1). The slight difference in the slopes, however, is not enough to infer that the mechanism of aging is different for the two sets of tires. On the contrary, the similarity of the slopes suggests that even though the tires are from two separate batches the mechanism of aging is the same for both sets of tires.
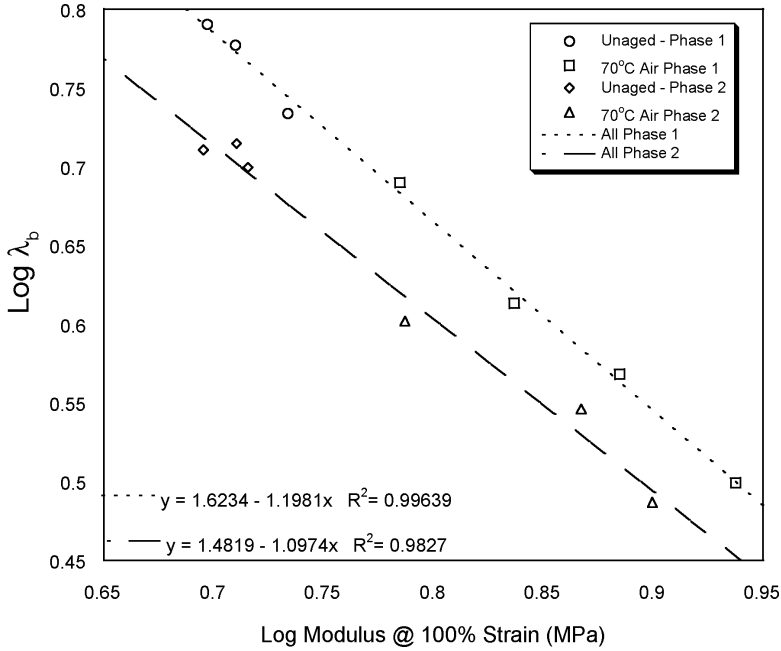

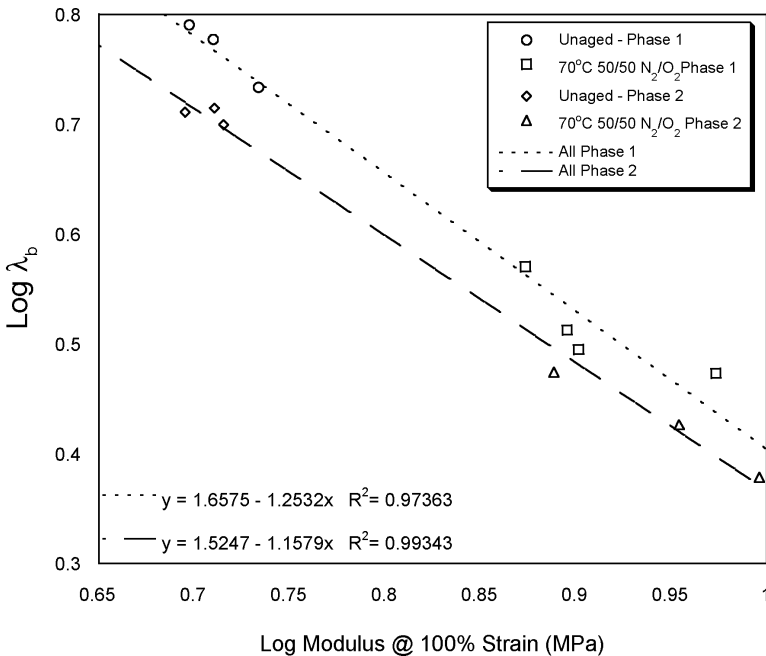FIG. 3. – Ahagon plot for tires from both phases, oven aged at 70 °C with air as the inflation media.

FIG. 4. – Ahagon plot for tires from both phases, oven aged at 70 °C with 50/50 N_2/O_2 as the inflation media.

An additional method used to compare the results of the two studies was to plot the normalized strain ratio at break vs. residence time in the ovens at 70 °C (Figure 5). Normalized strain ratio at break is determined by dividing the strain at break of a tire aged in the oven for time t ($\lambda_{b(t)}$) and dividing it by the strain at break for a new, unaged tire ($\lambda_{b(0)}$). The resulting regression lines in Figure 5 show that the relative change in properties vs. time for tires used in both studies are very similar and fall on the same curve. The difference between the two curves shown in Figure 5 is the inflation media used to pressurize the tire. Another conclusion that can be drawn from Figure 5 is that using a 50/50 blend of N_2/O_2 reduces the elongation at break in the wedge to much lower values than using air inflation.
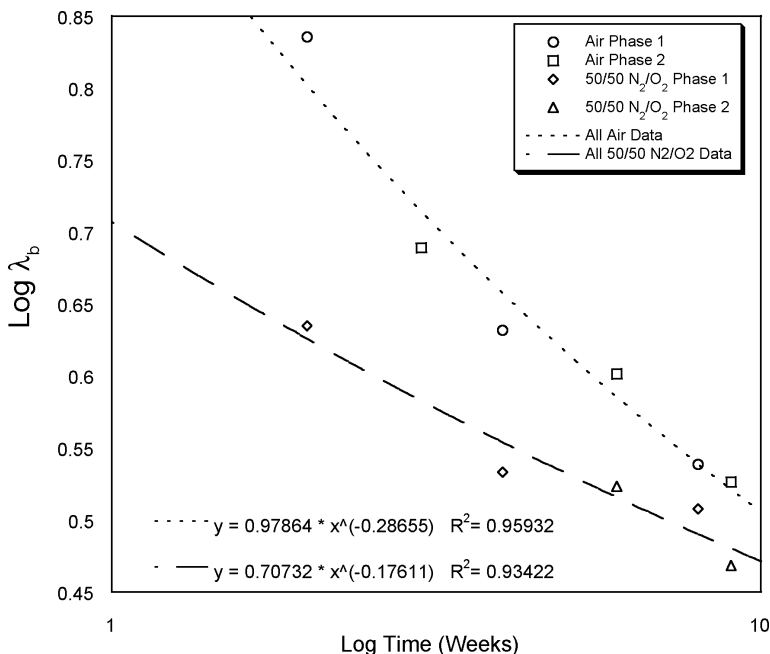

FIG. 5. – Normalized strain at break vs. time for tires from both phases of the study. Tires were aged in either air or 50/50 N_2/O_2.

The results from the data analysis performed on the tires aged at 70 °C allow one to conclude that the minor differences in initial properties of the tires in the two phases do not change the mechanism of aging and that normalization can be used to compare aging results.

Figures 6 and 7 are the 'Ahagon' plots for tires from Phase 1 and Figures 8 and 9 present data plotted in the same manner for tires from Phase 2. Using Figure 2 as a template for judging the aging mechanism, it appears that for Phase 1, 70 °C is the only temperature at which aerobic aging occurs, regardless of the inflation media. As the temperature is raised, the mechanism changes from Type I to Type III (high temperature aerobic) for 80 °C, to Type II (anaerobic) for 90 °C and 100 °C, again regardless of the inflation media. The mechanism of aging for Phase 2 data (oven aged temperatures between 40 °C and 70 °C) all appear to be aerobic, except for longer times at 60 °C and 70 °C with air as the inflation media. If one uses Figure 2 as a guide, the points at longer time would be considered aging according to the Type III high temperature mechanism. 60 °C and 70 °C, however, are conditions usually not considered 'high temperature'. The more likely reason for the deviation from linearity of these points is the change in the O_2 concentration in the pressure cavity of the tire over time. Measurements made on the contained

air O_2 concentration of the tires show that the change is from 20% O_2 concentration in the unaged tire to approximately 10% O_2 concentration in tires aged 9-12 weeks in the oven. As the concentration of O_2 passes below a critical point, molecular O_2 may not be making it to the wedge of the tire. The O_2 already reacted in at the wedge may undergo further reaction, possibly leading to chain scission, which mimics the Type III mechanism, leading one to the conclusion that the temperature was too high for aerobic aging. For these aging conditions, the O_2 concentration was too low for normal aerobic aging. This conclusion leads one to investigate the use of N_2 as an inflation media. If tires truly oxidize from the inside out and a reduction in O_2 concentration in the tire cavity can retard degradation, then N_2 inflation should be able to improve the durability of a tire.[16]
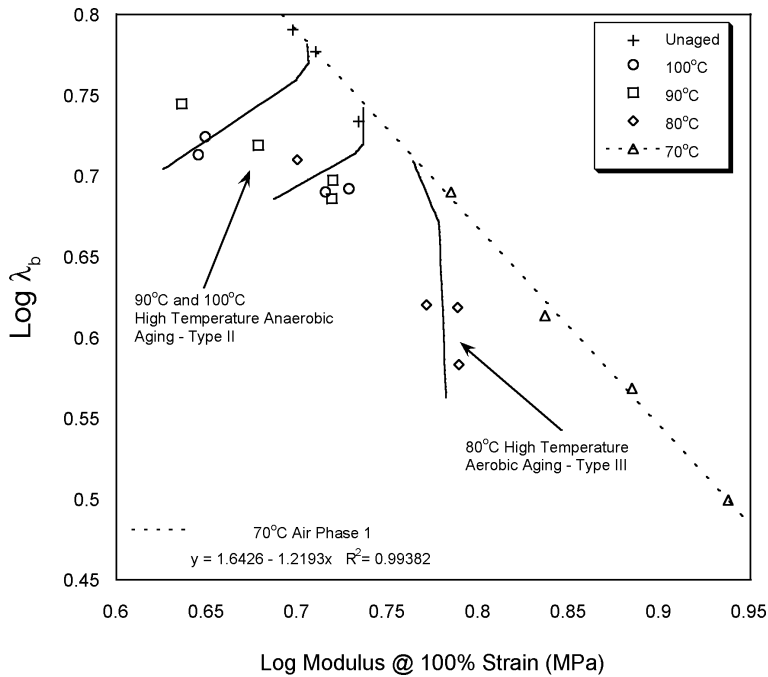

FIG. 6. − Ahagon plot for Phase 1 tires aged with air as the inflation media. Only 70 °C data aged aerobically.
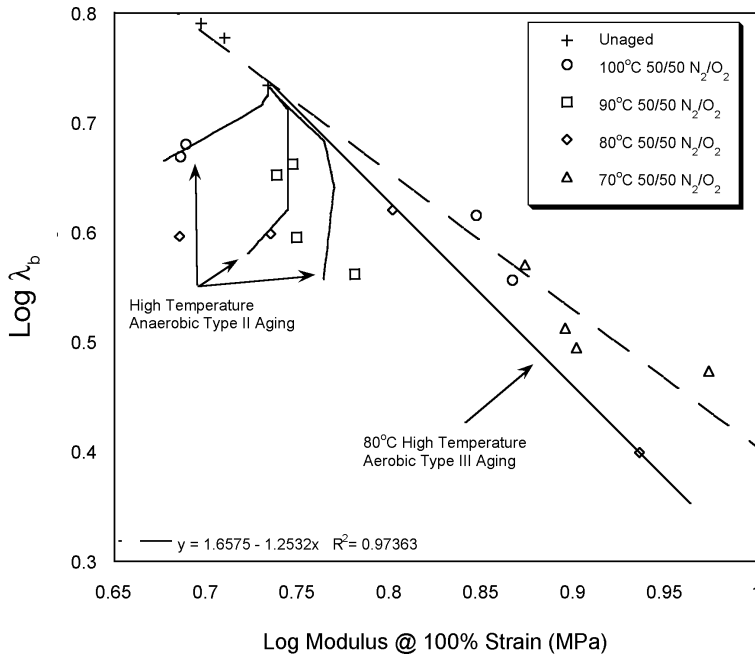
FIG. 7. – Ahagon plot for Phase 1 tires aged with 50/50 N_2/O_2
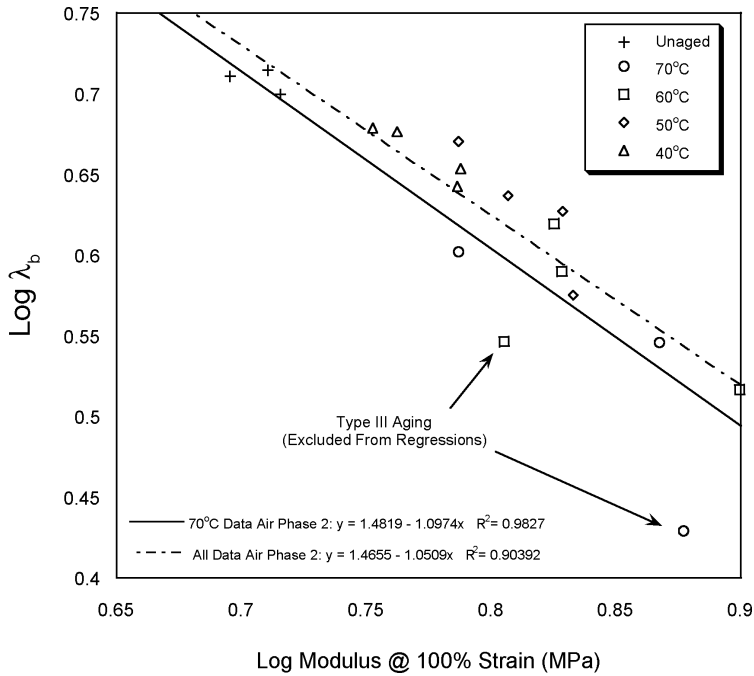as the inflation media. Only 70 °C data aged aerobically.

FIG. 8. – Ahagon plot for Phase 2 tires aged with air as the inflation media. Tires at all temperatures
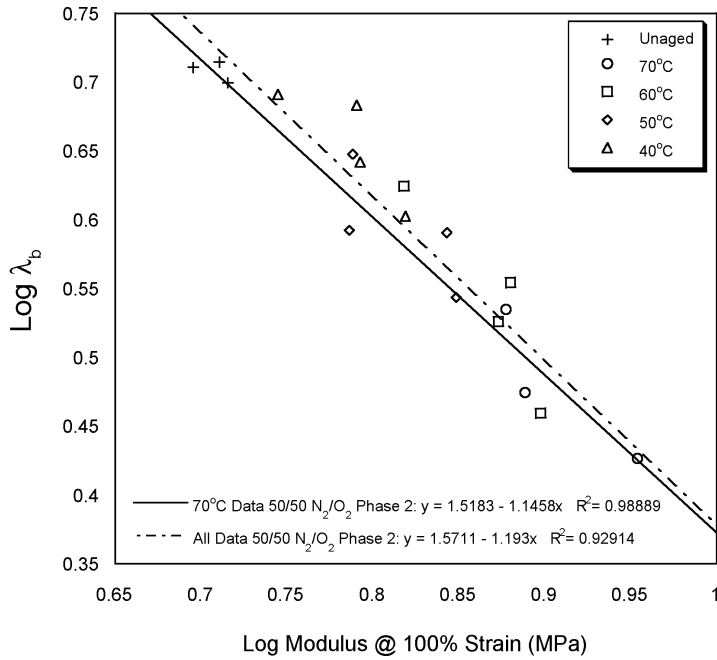aged aerobically. The only exceptions were at longer oven residence times for tires at 60 °C and 70 °C.

FIG. 9. – Ahagon plot for Phase 1 tires aged with 50/50 N_2/O_2
as the inflation media. All tires aged data aged aerobically.

Another method employed to analyze the tensile data obtained from the wedge rubber was that of Gillen, *et al.*,[7-9] who employed the classic time-temperature superposition approach using strain at break data. This method will be used here to analyze the kinetics of aging in order to determine both if the aging of the wedge rubber is diffusion limited and whether or not the results obey the Arrhenius equation. Arrhenius plots will be constructed using the shift factors (a_t) empirically determined from the plots of normalized strain ratio at break ($\lambda_{b(t)} / \lambda_{b(0)}$) vs. time. Figure 10 is a plot of the normalized strain-at-break vs. log time for the data from both studies (The data presented are for tires inflated with air. The data for the 50/50 N_2/O_2 inflated tires are almost identical and therefore are not shown).
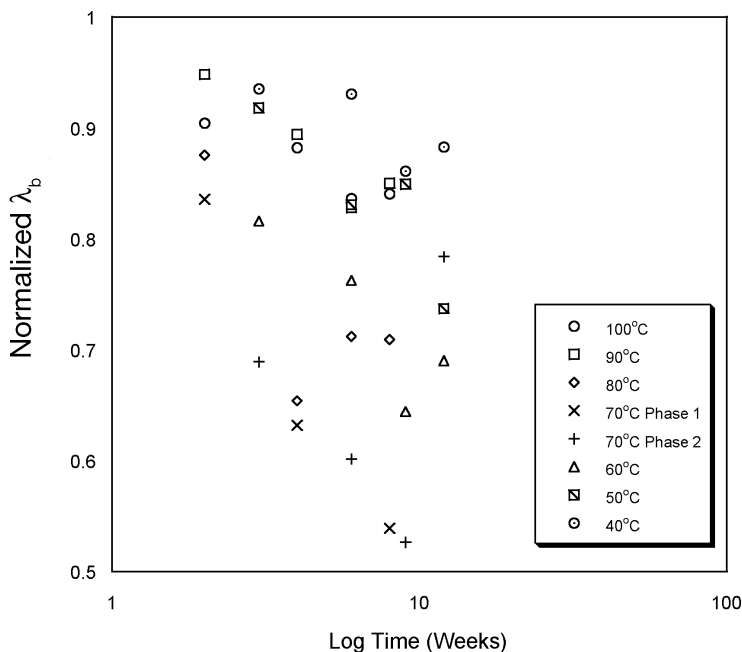
FIG. 10. – Normalized strain ratio at break vs. log time for all data from both phases of the study.

It is customary to shift the data along the X-axis from the higher temperatures on to the lowest temperature tested, in this case 40 °C. To help get the most accurate shift factors, the shifting was broken into two steps. Figure 11 is a graph of the Phase 2 data, shifted on to the 40 °C data. The data falls very nicely on a logarithmic regression line. Figure 12 is of the total data set shown in Figure 10, also shifted on to the 40 °C data. This data also falls on a logarithmic regression fit. It should be noted that the logarithmic fits were performed after the empirical shift factors were determined and are added to aid the reader's eye. The data for Phase 1 exhibits more scatter than Phase 2 data because of the change in aging mechanism at the higher temperatures. The plot of the shift factors (a_t) vs. the oven temperatures are shown in Figure 13. The data show a trend of increasing (a_t) from 40 °C to a peak at 70 °C, then (a_t) decreases from 70 °C down to 100 °C. Shift factors are the same as acceleration factors. The higher the acceleration factor (shift factor), the more degradation occurs per unit of time. As the temperature is increased from 40 °C to 70 °C, the degradation rate is accelerated. Past 70 °C, the degradation rate slows down. The reason the degradation rate slows over 70 °C is because of a condition known as diffusion limited oxidation (DLO). DLO becomes significant when the rate of oxygen consumption in the rubber is greater than the rate which oxygen can be resupplied through diffusion.[13] As the concentration of O_2 in the wedge rubber decreases, the rate of oxidation also decreases, since oxidation of NR is a first order reaction with respect to O_2 concentration.
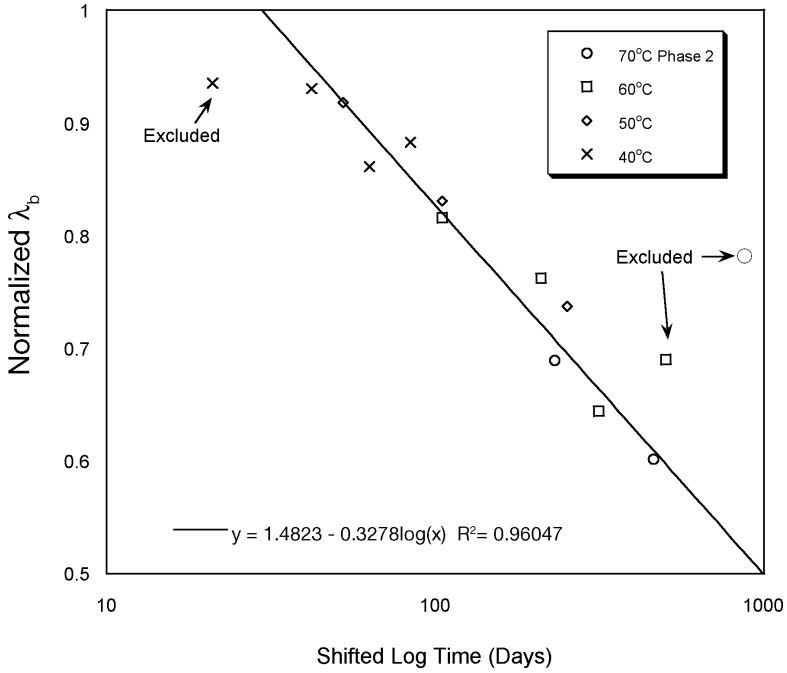
Fig. 11. - Normalized strain ratio at break vs. shifted log time for data from Phase 2.
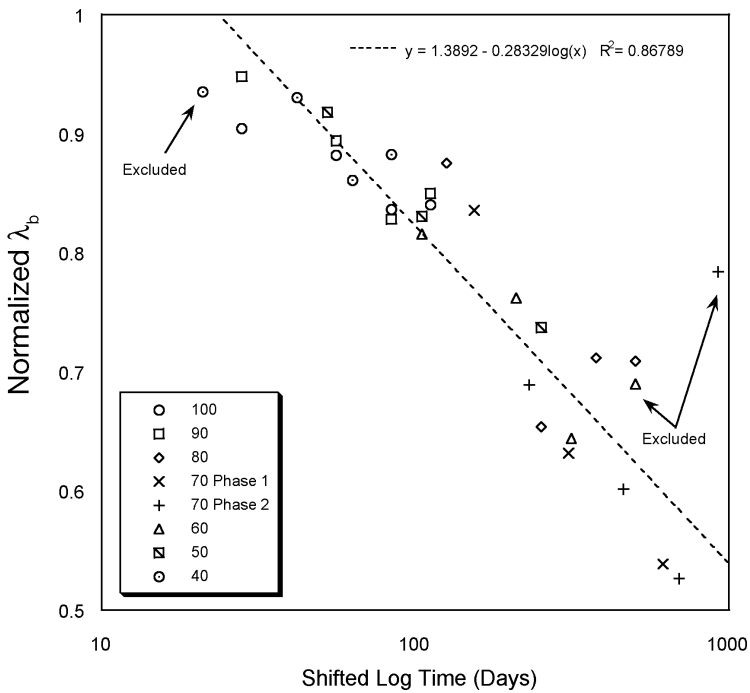Excluded data was not used to calculate the regression line.

Fig. 12. - Normalized strain ratio at break vs. shifted log time for all data from both phases.
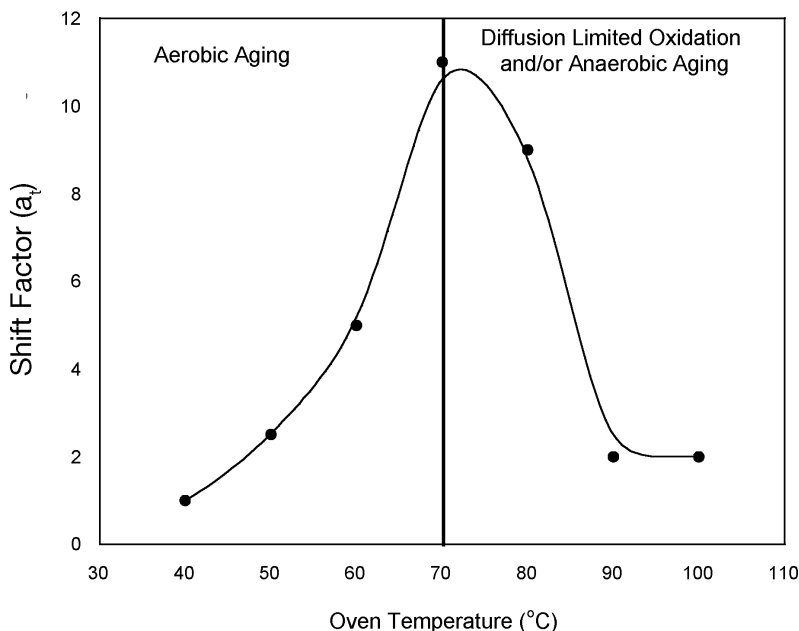Excluded data was not used to calculate the regression line.

FIG. 13. – Shift factors (determined from Figures 11 and 12) plotted against temperature.

In order to extract the apparent activation energy due to oxidation kinetics, ΔE_k, from the shift factors, it is necessary to understand and estimate the contributions of diffusional effects to the aging process. The process of O_2 diffusion can be reflected by an additional contribution to the overall apparent activation energy, ΔE, by an amount related to the activation energy for the diffusion of O_2, ΔE_d. An inherent assumption in determining how these quantities are calculated is the implication that a measured quantity (such as strain at break, for example) is related to the total amount of O_2 reacted into a sample. Given this assumption, one only needs to examine the O_2 flux, f_{O2}, at the surface of a semi-infinite slab:[17]

$$f_{O_2} = C_o(Dk)^{\frac{1}{2}} \tag{1}$$

where D and k are the diffusivity and first order rate constant for O_2, respectively. Inserting the Arrhenius temperature dependency for D and k results in:

$$f_{O_2} = C_o\left(D_o k_o\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E_k + \Delta E_d}{2RT}\right) = C_o\left(D_o k_o\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E}{RT}\right) \tag{2}$$

where, D_o, and, k_o, are pre-exponential factors, R, is the universal gas constant, and, T, is the temperature. Thus, a measured overall apparent activation energy can be related to the more fundamental diffusional and kinetic energies by:

$$\Delta E = \frac{\Delta E_k + \Delta E_d}{2} \tag{3}$$

Therefore, a plot of Log (a_t) vs. 1/T yields:

$$Slope = \frac{\Delta E_k + \Delta E_d}{2R} \qquad (4)$$

Figure 14 is a graph of Log (a_t) vs. 1/T for both air and 50/50 N_2/O_2 inflated tires. The temperatures used were from 40 °C to 70 °C (If a plot of the higher temperatures was used, negative activation energies would be the result.). The apparent activation energy (that is, the energy of activation calculated from just the value of the slopes from Figure 14) over this temperature range is ~70 kJ/mole for both inflation media. The value of ΔE_d for the diffusion of O_2 through natural rubber is known to be 34 kJ/mole.[18] Inserting the value of ΔE_d and the slopes from Figure 14 into Eq. 4 yields the correct energy of activation for the change in strain ratio vs. time. For air inflated tires the energy of activation is calculated to be 107 kJ/mole, and the energy of activation for 50/50 N_2/O_2 inflated tires is 105 kJ/mol. These values are in excellent agreement with the activation energies reported in the literature for the oxidation of crosslinked natural rubber.[19] This method of analysis confirms that the mechanism of aging for the wedge rubber in these tires is aerobic in the temperature range from 40 °C to 70 °C.
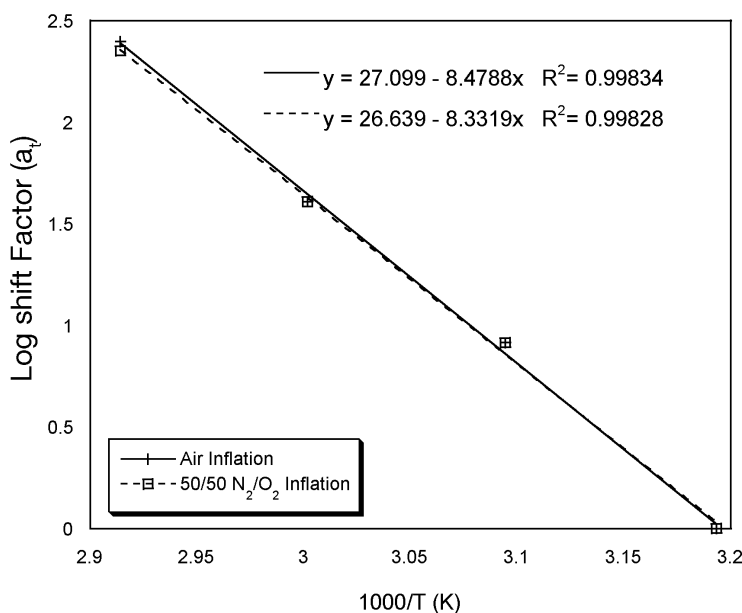

FIG. 14. – Arrhenius plot of the log shift factor vs. the inverse of temperature (in °K) for tires oven aged at 40 °C to 70 °C.

As stated in the Introduction section, this research is part of a larger effort to develop an accelerated aging test for new tires. The ideal test protocol would achieve two goals. First, after accelerated aging, tires would have chemical/physical properties identical to those found in actual field tires. The laboratory aging results for tires aged at temperatures ranging from 40 °C to 70 °C have been shown to age aerobically, the same mechanism as field aged tires. Second, the amount of test time could be varied (without changing other test parameters) to yield tires of any equivalent age desired. For example, 3 weeks at condition X yields a tire of equivalent field age Y, 5 weeks at condition X yields a tire of equivalent field age Z, *etc*. To accomplish the second goal, field data from used tires has to be tested and evaluated in the same way as the laboratory oven aged tires.

The field data for normalized strain ratio versus time in service are shown in Figure 15 for three different tire brands versus time in service in Detroit.[1] This data set is from vehicles classified as Sport Utility Vehicles (SUV). While there is significant variability in the field data, the normalized strain ratio clearly decreases with aging time. As discussed previously, the decrease in strain ratio correlates better with time in service than it does with mileage.[1] The tires do appear to age at different rates. In particular, Tire Brand C ages at less than half the rate of Tire Brand A. The field data for the different tire brands can be shifted onto the oven-aging curve as shown in Figure 16. The shape of the oven and field aging curves are indistinguishable suggesting that the aging mechanism is the same for both, aerobic. The shift factors relative to the 40 °C oven data are as follows: Tire Brand A = 0.44; Tire Brand B = 0.34; and Tire Brand C = 0.18. For Tire C, we can conclude that 6.5 days of aging at 70 °C in air is equivalent on average to 1 year of aging in Detroit. If the condition 50/50 N_2/O_2 at 70 °C is used, only 4.5 days is required to generate 1 year of field aging in Detroit. This laboratory is in the process of generating oven-aging data for other tire brands in order to compare to the field data for Detroit, along with other cities such as Phoenix in order to determine the correlation between field and oven aging for different brands and tire types.
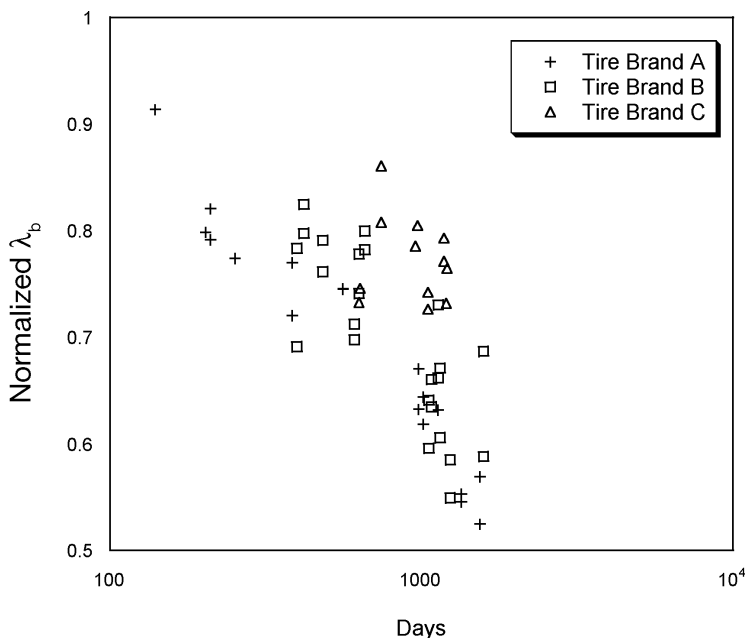

FIG. 15. - Normalized strain ratio at break vs. log time for 3 brands of field aged SUV tires.[1]
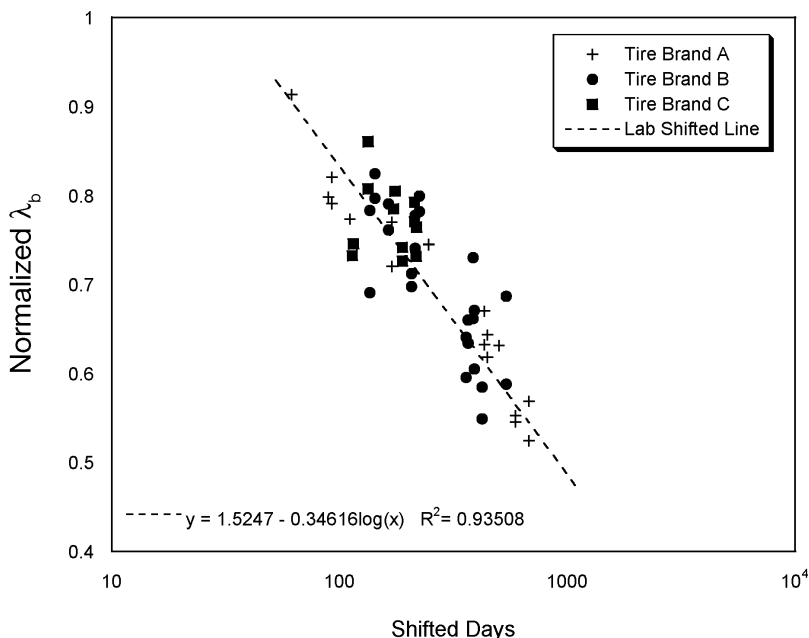
FIG. 16. - Normalized strain ratio at break vs. shifted log time for three brands of field aged SUV tires.
The data for the field aged tires has been shifted on to the curve from Figure 11.
Figure 11 was chosen because the data scatter was low.

Based on long-term average ambient temperature data together with the apparent activation energy of 70 kJ/mole from the oven data, it is possible to compute an Arrhenius weighted average temperature for Detroit of 14 °C. As shown in Figure 17, the field aging rate for tire C falls above the extrapolated line by a factor of ~2. That is, tires in Detroit age roughly 2 times faster than would be predicted by oxidation at ambient Detroit temperatures. The other tire brands fall even higher above the extrapolated line.

There are several possible reasons why tires might age faster in the field than predicted by the oven aging results. The most straightforward explanation is that tires experience higher than ambient temperatures due to heating from sun load and driving. Road surfaces can be up to 20 °C hotter than ambient temperatures due to sun load. We expect that the sun load effect on a tire will be similar. Sun load can increase tire temperatures over ambient for up to 8 hours/day. It is important to note that parking habits (fraction of time parked in the shade, parking orientation and so on) will affect the contribution of sun load to increased oxidative dose. Depending on speed, load, and inflation pressure, "normal" driving can increase tire temperatures above ambient by 10-50 °C, especially in the wedge area of the tire, where the tensile measurements were made. Vehicles are typically driven around 2 hours/day. Estimates of average sun load dose and driving are consistent with an observed increase in rate above that predicted for ambient temperatures of about a factor of 2. It is also possible that particular tires run hotter than others. This may, in part, explain the different field aging rates for the different tire brands. Since different tires experience different temperature histories under the same ambient conditions, it is not surprising that tire aging varies more in the field than in the oven tests. In fact, the expected variation in sun load and driving habits is sufficient to account for the observed variability in the field tire aging results. Of course, other noise factors, such as differences in compounding philosophy and variations from batch-to-batch in initial properties (which would affect the normalization), will also contribute. Additional field data will be obtained from other cities so that more detailed

comparisons with oven aging can be made. This data will be discussed in a future report.
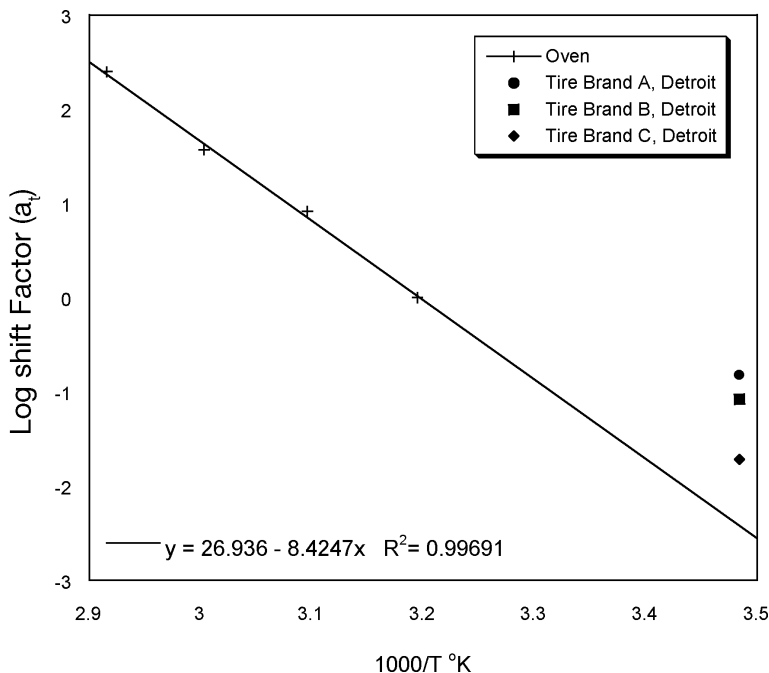

FIG. 17. - Arrhenius plot of the log shift factor vs. the inverse of temperature (in °K) for tires oven aged at 40 °C to 70 °C (air inflation), along with the shift factors from the field aged tires.

CONCLUSIONS

1) By using the methods of both Ahagon and Gillen, it has been shown that the wedge rubber of tires oxidatively ages at oven temperatures between 40 °C and 70 °C when mounted and inflated with either air or a blend of 50/50 N_2/O_2.

2) At oven temperatures between 40 °C and 70 °C, the degradation rate of the wedge rubber increases with increasing temperature. Above 70 °C the degradation rate slows down. The reason the degradation rate slows over 70 °C is because of a condition known as diffusion limited oxidation (DLO).

3) Including the energy of activation for O_2 diffusion in the calculation of the Arrhenius activation energies allows for a more precise estimate of the energy of activation of oxidation to be made.

4) The use of the field data obtained in an earlier study permits the calculation of shift factors (acceleration factors) for the oven aging properties being measured.

5) The shape of the field data curve when shifted onto the oven aging curve suggests the aging mechanism of the wedge rubber for all the tires investigated is aerobic.

6) It appears from the data that field aged tires oxidize at a faster rate than simply the ambient temperature. This suggests that the tires are actually hotter than ambient, which can be accounted for by both sun load and operation, both of which increase the temperature of the tire.

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